Structural Mechanism of The Lattice Thermal Expansion of β-eucryptite: A Combined Synchrotron X-ray and Neutron Rietveld Analysis	X7A

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The structures of ordered and disordered β-eucryptite have been determined from Rietveld analysis of powder synchrotron X-ray and neutron diffraction data over a temperature range of 20 to 873 K. On heating, both materials show an expansion within the (001) plane and a contraction along the **c**-axis. However, the anisotropic character of the thermal behavior of ordered β-eucryptite is much more pronounced than that of the disordered compound: The linear expansion coefficients of the ordered and disordered phases are $\alpha_a = 7.26 \times 10^{-6}$ K^{-1}; α_c = -16.35 $\times 10^{-6}$ K^{-1}, and $\alpha_a = 5.98 \times 10^{-6}$ K^{-1}; α_c = -3.82 $\times 10^{-6}$ K^{-1}, respectively. The thermal behavior of β-eucryptite can be attributed to three interdependent processes that all cause an increase in a but a decrease in c at higher temperatures: (1) Si/Al tetrahedral deformation, (2) Li positional disordering, and (3) tetrahedral tilting. Because disordered β-eucryptite does not exhibit tetrahedral tilting, the absolute values of its axial thermal coefficients are smaller than those for the ordered sample.

At low temperatures, both ordered and disordered β-eucryptite exhibit a continuous expansion parallel to the **c**-axis with decreasing temperature, while a remains approximately unchanged. Our difference Fourier synthesis reveals localization of Li ions below room temperature, and we suggest that repulsion between Li and Al/Si inhibits contraction along the **a**-axes.